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(54) Title: CROSS-LINKED ACRYLATE COATING MATERIAL USEFUL FOR FORMING CAPACITOR DIELECTRICS AND OXYGEN BARRIERS



(57) Abstract

Sheet material is given low oxygen permeability or prepared for winding high voltage capacitors by evaporating polyfunctional acrylate monomer having a molecular weight in the range of 150 to 600 and condensing the acrylate as a monomer film on a dielectric or thermoplastic substrate (23). The acrylate is polymerized by irradiation by ultraviolet or electrons. A metallized layer (24) provides an electrode of a capacitor. Electrical contact can be made by Schooping even though the metallized layer is covered by a layer of acrylate (26). A material selected from silicon oxide, silicon nitride, aluminum nitride, titanium nitride, aluminum oxide, and metal may be deposited for forming an oxygen barrier. Adhesion is enhanced by plasma treatment of a surface immediately before deposition. Condensation efficiency is also enhanced by chilling the substrate on which the acrylate is condensed.

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**CROSS-LINKED ACRYLATE COATING MATERIAL USEFUL FOR FORMING
CAPACITOR DIELECTRICS AND OXYGEN BARRIERS**

Background

This invention relates to deposition of barrier films for inhibiting penetration by oxygen or other gases. It also relates to high-voltage capacitors and the material employed for fabricating such capacitors. Techniques for acrylate deposition and adhesion are also improved.

Many products, including many food products, are packaged in thin plastic sheet bags or the like. The thin films are desirably resistant to permeation by oxygen, water vapor and odorous gases.

Such barrier films are commonly made of costly plastics because less costly films are too permeable to oxygen or water to give a long shelf life. Reduced cost barrier films are highly desirable.

There are many products that are packaged in plastic bottles, tubes or vials which also need protection from oxidation or contamination by environmental gasses or which must be in impermeable containers so that components of the contents are not lost by diffusion through the containers.

Electrical capacitors are used for storing energy in a variety of applications. Operating voltages for such devices range from a few volts, such as those used in miniature electronic circuits, to thousands of volts, such as those used in power utility applications.

For low and medium voltages (generally below 600 volts) metallized sheet dielectrics are commonly used. Higher voltage capacitors are generally constructed of aluminum foil electrodes and sheet dielectric material such as a thermoplastic polypropylene and polyester film. Capacitors intended for service at more than about 600 volts are completely impregnated with a dielectric liquid with good gas absorbing properties. Typical dielectric liquids with good gas absorbing properties are PXE (phenyl xylyl ethane), MIPB (mono isopropyl biphenyl), DOP (dioctyl phthalate), castor oil, polypropylene glycol and mineral oil.

High voltage capacitors have not been able to take advantage of the self healing properties of metallized electrodes. The dielectric liquid causes swelling of the thermoplastic sheets, which causes cracking of the thin film metal electrode and an open circuit quickly develops. It would be desirable to have wound capacitors made with metallized film for higher voltages where self healing can occur, and often where it is necessary that the capacitor be liquid filled.

Brief Summary of the Invention

There is, therefore, a barrier with low oxygen and water permeability having a thermoplastic substrate, a cross-linked acrylate layer on one face of the substrate and a layer of oxygen barrier material deposited on the same face of the substrate as the acrylate layer, preferably over the acrylate layer, or in some embodiments, under the acrylate layer. In one

1 embodiment, the acrylate layer is a polymerization product of an acrylate monomer having
a molecular weight in the range of from 150 to 600. Alternatively, the acrylate layer may
be formed from a photopolymerizable acrylate that is sufficiently low viscosity to be sprayed
on the substrate or applied by dipping. Preferably, there is another cross-linked acrylate
5 layer over the oxygen barrier layer. It is preferable to deposit a top acrylate layer over a
metallized layer before the metallized layer contacts any surfaces.

The surface of the thermoplastic substrate is prepared for deposition of the acrylate
by either heating the surface of the substrate above its melting point without deforming the
substrate or by plasma treating the surface for enhancing adhesion of the acrylate. Chilling
10 the substrate enhances deposition efficiency.

It has also been discovered that metallized capacitor electrodes may be protected from
damage by corrosion or by dielectric liquids by applying coatings of resistant polymers on
one or both faces of the dielectric. Thus, there is a sheet material suitable for winding a
metallized sheet capacitor employing as a substrate a thermoplastic dielectric sheet. A
15 conductive metal layer is deposited on at least one face of the dielectric sheet. One layer of
polymerized acrylate is formed on the same face of the dielectric sheet as the conductive
layer, and another layer of polymerized acrylate may be formed on the opposite face of the
dielectric sheet.

The acrylate layers are formed by evaporating an acrylate monomer having a
20 molecular weight in the range of from 150 to 600, preferably in the range of from 200 to
400, and condensing the monomer on a face of the sheet substrate as a monomer film. The
acrylate monomer is then polymerized for forming the acrylate layer. Modifying the surface
of the dielectric sheet for increasing its surface energy, preferably by plasma treatment,
enhances curing or polymerization of the film by an electron beam or ultraviolet radiation.

25

Brief Description of the Drawings

FIG. 1 illustrates schematically a metallized sheet capacitor constructed according to
principles of this invention.

FIG. 2 illustrates in three transverse cross sections materials suitable for winding a
30 capacitor, FIG. 2a illustrating two coated sheets as used in a capacitor, FIG. 2b illustrating
a sheet coated on only one face, and FIG 2c illustrating a sheet with the coating sequence
reversed.

FIGs. 3, 4 and 5 illustrate, in fragmentary transverse cross section, other embodiments
of material suitable for winding capacitors.

FIG. 6 is a schematic illustration of coating apparatus for forming such a capacitor
35 sheet material.

FIG. 7 is a graph with the axes representing acrylate shrinkage and layer thickness,
respectively.

FIG. 8 is a graph illustrating condensation efficiency as a function of temperature.

40 FIG. 9 is a fragmentary cross section of a capacitor made with metallized sheet coated
with a polymerized acrylate.

1 FIG. 10 illustrates in transverse cross section a coated polypropylene with low oxygen permeability.

FIG. 11 illustrates in transverse cross section a coated thermoplastic substrate with low oxygen permeability.

5 FIG. 12 illustrates an exemplary container constructed according to principles of this invention.

FIG. 13 is a schematic illustration of apparatus for coating substrates by spraying.

FIG. 14 is a schematic illustration of coating apparatus for forming a barrier sheet material.

10 Description

An exemplary capacitor 10 comprises a can 11, the end of which is cut away in FIG. 1 to show the roll of capacitor material 12 inside the can. The layers of material forming the capacitor are wound into a cylindrical roll. In effect, the roll of capacitor material comprises alternating layers of metal and dielectric coiled in a tight spiral. The metal layers form the electrodes of the capacitor and the dielectric material between the electrodes permits accumulation of charge in the capacitor. Such a capacitor, intended for use at higher voltages, may be filled with a dielectric liquid such as those mentioned above.

15 FIG. 2 illustrates in three fragmentary transverse cross sections exemplary materials for winding such a capacitor. A sheet suitable for winding a capacitor has a thermoplastic substrate 13 such as thin polypropylene or polyester sheet which has a stable dielectric constant and high dielectric strength. A layer of metal 14 which may be vacuum deposited or sputtered is formed on at least one face of the substrate. A layer of polymerized acrylate 16 is deposited either over or under the metal layer as described hereinafter. In the embodiment illustrated in FIG. 2a, another layer of polymerized acrylate 17 is formed on the opposite face of the substrate.

20 The two sheets of material suitable for forming a capacitor are illustrated in FIG. 2a as they are sometimes used in capacitors. Each sheet has a portion of the metallized layer 14 exposed along an edge of the sheet. That is, a portion of the metallized layer is not covered by an insulating layer of acrylate in this embodiment. These exposed edges of the metal layer are at opposite edges of adjacent sheets in the capacitor and provide an area to which electrical contact can be made so that alternate sheets of the capacitor material form the opposite plates of the capacitor.

25 FIG. 2b illustrates another embodiment of sheet for forming a rolled capacitor. Here a layer of metal 14 is deposited on the substrate 13 and a layer of polymerized acrylate 16 is formed over the metal layer. The entire metal layer is covered with acrylate. Only one face of the substrate has a coating of acrylate.

30 The embodiment illustrated in FIG. 2c reverses the layers on the substrate. In this embodiment there is a layer of polymerized acrylate 16 formed directly on the substrate 13. In direct contact with and over the acrylate layer is a deposited layer of metal 14. Again, there is no acrylate layer on the opposite face of the substrate. The metal may extend all the

1 way to each edge of the sheet or may be spaced a short distance from the edge of the sheet
along one edge.

FIG. 3 illustrates a variation of the capacitor material having a layer of polymerized
acrylate 18 on each face of a thermoplastic substrate 19. A layer of metal 21 is deposited
5 on top of one of the acrylate layers.

FIG. 4 illustrates another slight variation from an embodiment as illustrated in FIG.
3, having a layer of polymerized acrylate 22 on each face of a substrate 23. A layer of metal
24 is deposited over at least one of the acrylate layers. A third layer of polymerized acrylate
26 is formed over the layer of metal. Any of these variations may be used for forming
10 capacitors.

It is not always required that a capacitor be formed with both electrodes being
metallized sheets of dielectric material. Thus, for example, as illustrated in FIG. 5, a
capacitor may have one electrode formed on a thermoplastic substrate 27. A layer of
polymerized acrylate 28 is formed on each face of the substrate. A layer of metal 29 is
15 deposited for forming the one electrode. The other electrode in such a capacitor comprises
a sheet of aluminum foil 31. That electrode may be separated from an adjacent layer of
metal (not shown) on another substrate via a sheet 32 of dielectric materials such as poly-
propylene.

As mentioned above, the polypropylene and polyester materials are desirable as
20 dielectrics for capacitors since they have a stable dielectric constant and high dielectric
strength. If a metallized polypropylene, for example, is tried in a liquid filled capacitor, the
thermoplastic apparently swells and ruptures the thin metallized layer. By having a very thin
layer of polymerized acrylate in direct contact with the metallized electrode, the damage
caused by dielectric liquid can be avoided. It is believed that the thermoset acrylate supports
25 or stabilizes the metal film and prevents cracking despite swelling of the film substrate.

If the acrylate layer is over the metal layer, it protects the metal layer from corrosion.
Although it does not appear to be necessary for forming certain capacitors, if both faces of
the dielectric sheet are coated with a layer of cured acrylate, the polymer film between the
layers is isolated from dielectric liquid in a capacitor, and swelling is avoided.

30 An exemplary barrier material as illustrated in FIG. 11 comprises a thermoplastic
substrate 110 having a cross-linked acrylate layer 111 on one face. The acrylate layer is
overlain by a layer 112 of oxygen barrier material. A final cross-linked acrylate layer 113
is optionally formed over the oxygen barrier layer.

It has been discovered that polyethylene, polypropylene, polyester or nylon substrates
35 with thin surface coatings of crosslinked acrylate have very low oxygen and water
permeability when combined with a metal or inorganic barrier coating. Typical sheets for
packaging foodstuffs include metallized polypropylene, nylon or polyester sheet. Metallized
nylon has an oxygen permeability of about 0.05 ml/100 in²/hour (ml/645 cm²/hour) as
measured with a Mocon Oxtran System available from Modern Controls, Minneapolis,
40 Minnesota. Metallized polyester has a typical oxygen permeability of about 0.08. Metallized
polypropylene, on the other hand, has an oxygen permeability of about 2.5 and is not usually

1 suitable for packaging where low oxygen permeability is important.

It is believed that the high oxygen permeability of metallized polypropylene is due to the inherent surface roughness of the polypropylene sheet. Nylon and polyester sheets are considerably smoother and have a higher temperature capability than polypropylene. A metal
5 coating of uniform thickness can be readily applied as a good oxygen barrier. A layer of acrylate about 1/2 to one micrometer thick is adequate for smoothing the surface for producing a low oxygen permeability.

Sheet polypropylene without any coating may have an oxygen permeability of about 100. However, if a layer of aluminum is applied to a surface of a polypropylene sheet
10 substrate, the oxygen permeability decreases to about 2.5. Surprisingly, when an acrylate layer only about one micrometer thick is formed on the polypropylene and then covered with a layer of metal, the oxygen permeability drops to about 0.05, a value lower than metallized polyester. It is hypothesized that the film of liquid acrylate monomer deposited on the surface of the polypropylene has a smooth, high temperature surface and the surface remains
15 smooth when the acrylate is polymerized. The metallized layer can then form a good oxygen barrier.

First, a layer of acrylate monomer is deposited on the substrate and crosslinked. The acrylate layer is then coated with an oxygen barrier layer of SiO_x or Al_2O_3 , both of which have good resistance to oxygen permeability. The high temperature resistance of the
20 crosslinked acrylate layer permits the notably higher temperature deposition of silicon oxide or aluminum oxide on the thermoplastic substrate. Other deposited barrier films may be formed of nitrides or silicides that can be vacuum or vapor deposit. For example, silicon nitride, aluminum nitride, or titanium nitride may be used. The materials need not be stoichiometric compounds and often are substoichiometric with excess metal.

A still greater surprise occurs when another polymerized acrylate layer is formed over the oxygen barrier layer. The permeability through a polypropylene barrier material drops to about 0.002 which is appreciably better than the oxygen permeability of metallized nylon. It is hypothesized that the second acrylate layer may protect the metallized layer and assure retention of the oxygen barrier properties of the metal.

A preferred composite material with low oxygen permeability has a layer of
30 polymerized acrylate, a layer of barrier material such as SiO_x , Al_2O_3 , silicon nitride, titanium nitride or aluminum nitride and another layer of polymerized acrylate on a thermoplastic substrate. The layers of acrylate reduce permeability dramatically and the layer overlying the barrier material protects the barrier material from mechanical damage and also provides
35 a surface suitable for printing.

The substantial improvement in oxygen permeability is believed to be attributable to formation of a liquid film of monomer on the surface of the polypropylene, followed by cross linking of the polyfunctional acrylate. Adding a second layer of acrylate monomer which is polymerized in situ is believed to rectify any defects in the underlying layers and provide an
40 additional thickness of material with inherently low oxygen permeability. Redundant layers minimize pinhole leakage.

1 A particularly useful barrier sheet may be formed with multiple layers of acrylate and
oxygen barrier. Several thin layers of such materials are more effective than a couple thicker
layers with the same total thickness. For example, a sheet may be coated with a layer of
5 cross linked acrylate about 0.5 micrometers thick followed by a layer of metal or other
oxygen barrier about 0.1 micrometer thick. Subsequent layers of acrylate and metal are built
up, preferably with the final layer being acrylate. The thin layers of acrylate between layers
of metal reduce the lateral flow of oxygen in the layers and minimize permeability. Such an
arrangement is particularly useful as an oxygen barrier on bottles or vials.

10 Although it is generally preferred to deposit a layer of acrylate on the substrate,
followed by a layer of oxygen barrier material, oxygen permeability can be sharply reduced
with a layer of metal deposited directly on the substrate, followed by a layer of acrylate.

The polymerized acrylate layer is believed to be beneficial for a number of other
reasons. As a thermoset material, it has higher temperature resistance than the thermoplastic
substrate. In the coating process, the product is subjected to elevated temperature processing
15 such as metallizing, plasma treatment and the like. A cured acrylate coating would not have
vapor emissions and may seal the surface and inhibit emission of materials from a
thermoplastic substrate.

It is particularly preferred to vaporize an acrylate prepolymer and deposit it on a
substrate in a vacuum system since this technique serves to refine the acrylate. In effect, the
20 vaporization and deposition process is a vacuum distillation which removes volatiles to the
vacuum pumps and deposits only higher molecular weight acrylates on the substrate.
Removal of volatiles is desirable for subsequent high temperature processing of the material
such as in deposition of metal or other inorganic barrier films.

25 After any of these deposition techniques, the monomer film is irradiated with
ultraviolet or an electron beam to cause polymerization of the acrylate to form a monolithic
crosslinked layer. Polymerization by irradiation is a conventional practice and the electron
flux required or wavelength and total flux of ultraviolet used are commonly known. A
photoinitiator may be included in the acrylate for facilitating polymerization by ultraviolet
radiation.

30 A suitable apparatus for coating the substrate with acrylate and metal layers is
illustrated schematically in FIG. 6. All of the coating equipment is positioned in a
conventional vacuum chamber 36. A roll of polypropylene, polyester or nylon sheet is
mounted on a pay-out reel 37. The sheet 38 forming the substrate is wrapped around a first
rotatable drum 39, around a second rotatable drum 40, and fed to a take-up reel 41. Idler
35 rolls 42 are employed, as appropriate, for guiding the sheet material from the payout reel to
the drums and to the take-up reel.

A flash evaporator 43 is mounted in proximity to the drum at a first coating station.
The flash evaporator deposits a layer or film of acrylate monomer on the substrate sheet as
it travels around the drum. After being coated with acrylate monomer the substrate sheet
40 passes an irradiation station where the acrylate is irradiated by a source 44 such as an
electron gun or source of ultraviolet radiation. The radiation or electron bombardment of

1 the film induces polymerization of the acrylate monomer.

The sheet then passes a metallization station 46 where a coating of metal for an electrode is applied by vacuum metallizing or sputtering. The sheet then passes another flash evaporator 47 where another layer of acrylate monomer is deposited for forming a protective layer over the metal. This layer of monomer is cured by irradiation from an ultraviolet or electron beam source 48 adjacent the drum. Depending on whether a layer of acrylate is above or below the metal layer, either of the evaporators 43 or 47 may be used. Clearly, if the metal layer is to be sandwiched between layers of acrylate, both evaporators and their respective radiation sources are used.

10 An exemplary process for coating a container can be described as follows. The container is injection molded or blow molded in a conventional manner from a conventional thermoplastic material. Preferably the container is then flame treated for activating and smoothing the surface. It has been found that adhesion of an acrylate layer on the substrate is enhanced by activating the surface by plasma or flame treating. High temperature air may also be used.

In a typical production line, a row of containers 114 are moved successively through a flame treating station, a coating station and a curing station. In the flame treating station, the containers are bathed in the flames from a plurality of propane or natural gas torches 116. In addition to activating the surface for enhanced adhesion, the flame treating can significantly smooth the surface of the container to assure that there is complete coverage by subsequent coatings. The flame is applied to the surface with sufficient intensity to soften or melt a thin surface layer on the container.

The flame treatment melts and rounds off any molding flash and smooths mold marks on the container so that the coating can bridge surface irregularities. "Melting" may almost be considered a misnomer since the thermoplastic materials are effectively supercooled liquids. Thus, melting is considered to be sufficient softening of the surface for smoothing irregularities.

Such an acrylate layer is applied in a coating station where one or more nozzles 17 sprays a thin coating of acrylate monomer onto the surface. Such a sprayed coating may be in the order of from one to twenty micrometers thick, for example. The acrylate sprayed onto the surface may be a low viscosity monomer or if desired, a monomer and/or a low molecular weight polymer may be combined with a solvent for spraying. In the event the acrylate is to be cross-linked by ultraviolet irradiation, a photoinitiator may be included in the sprayed composition.

35 An alternative to spraying the surface of the container with acrylate comprises dipping the container into a liquid acrylate composition.

Following the coating station, the containers pass a curing station where a plurality of ultraviolet lamps 18 irradiate the acrylate layer and cause cross-linking.

40 Following the application of an acrylate layer to the containers, an oxygen barrier layer is applied. Preferably this is by deposition in a vacuum chamber. A metal barrier layer, e.g. aluminum, may be applied by vacuum metallizing or sputtering. A layer of

1 silicon oxide, aluminum oxide, silicon nitride or other such material may be deposited by a
plasma assisted chemical vapor deposition technique. For example, SiO_x may be deposited
by a plasma vapor deposition process using an oxidizing or inert carrier gas. Aluminum
oxide can be deposited by electron beam evaporation or preferably by evaporation of
5 aluminum which is converted to an oxide in an oxygen plasma.

An alternative technique for depositing an acrylate layer is in a vacuum chamber.
Suitable apparatus for coating a sheet substrate with acrylate and oxygen barrier layers is
illustrated schematically in FIG. 14. All of the coating equipment is positioned in a
conventional vacuum chamber 121. A roll of polypropylene, polyester or nylon sheet is
10 mounted on a pay-out reel 122. The sheet 123 forming the substrate is wrapped around a
rotatable drum 124 and fed to a take-up reel 126. Idler rolls 127 are employed, as
appropriate, for guiding the sheet material from the payout reel to the drum and to the take-
up reel.

A flash evaporator 128 is mounted in proximity to the drum at a first coating station.
15 The flash evaporator deposits a layer or film of acrylate monomer on the substrate sheet as
it travels around the drum. After being coated with acrylate monomer the substrate sheet
passes an irradiation station where the acrylate is irradiated by a source 129 such as an
electron gun or source of ultraviolet radiation. The UV radiation or electron bombardment
of the film induces polymerization of the acrylate monomer.

20 The sheet then passes a deposition station 131 where a coating of oxygen barrier
material is applied by plasma deposition, vacuum deposition or the like. The sheet then
passes another flash evaporator 132 where another layer of acrylate monomer is deposited
for forming a protective layer over the oxygen barrier. This layer of monomer is cured by
irradiation from an ultraviolet or electron beam source 133 adjacent the drum. The coated
25 sheet is then wrapped up on the take-up reel 126.

Evaporation of the monomer is preferably from flash evaporation apparatus 129, 132
as described in U.S. Patents Nos. 4,722,515, 4,696,719, 4,842,893, 4,954,371 and/or
5,097,800. These patents also describe polymerization of acrylate by radiation. In such
flash evaporation apparatus, liquid acrylate monomer is injected into a heated chamber as
30 droplets. The elevated temperature of the chamber vaporizes the droplets to produce a
monomer vapor. The monomer vapor fills a chamber with a longitudinal slot forming a
nozzle through which the monomer vapor flows.

Two styles of evaporator are suitable. In one of them, the orifice for injecting
droplets and flash evaporator are connected to one end of the nozzle cylinder. In the other
35 style, the injector and flash evaporator section is attached in the center of the nozzle chamber
like a T.

It is often found desirable to plasma treat the surface to be coated immediately before
coating. A conventional plasma gun 134 is positioned in the vacuum chamber upstream from
each of the flash evaporators 128 and 132 for activating the surface of the sheet on a
40 continuous basis before monomer deposition. Conventional plasma generators are used.

Surface treatment within the vacuum chamber is of substantial importance for all

1 surfaces, not just the surface of the raw film. Referring again to FIG. 6, a conventional
plasma gun 52 is positioned in the vacuum chamber upstream from each of the flash
evaporators 43 and 49 for activating the surface of the sheet on a continuous basis before
monomer deposition. Another plasma gun 52 is provided immediately before the vacuum
5 metallizing station 46. Conventional plasma generators are used.

In an exemplary embodiment the plasma generator is operated at a voltage of about
500 to 1000 volts with a frequency of about 50 KHz. Power levels are in the order of 500
to 3000 watts. For an exemplary 50 cm wide film traveling at a rate of 30 to 90 meters per
minute, around 500 watts appears appropriate.

10 An analogous system may be employed for coating containers with layers of acrylate
and barrier material. The containers are moved successively through an acrylate evaporation
and condensation station and a deposition station. If two layers of acrylate are used the
second acrylate may be applied by way of the same flash evaporator or by way of a second
similar flash evaporator.

15 The acrylates used for forming the cross-linked coatings on the thermoplastic substrate
differ somewhat depending on the technique used for depositing the coating. The acrylates
used for dipping or spraying are similar and it is not necessary that the acrylate is a
monomer. Generally, the acrylates used are blends of high and low molecular weight
materials to yield the desired viscosity of the composition for dipping or spraying.
20 Monomers with molecular weights in the order of 150 up to partially polymerized materials
have a molecular weights in the order of 20,000 may be blended to obtain a low viscosity
blend. There should be polyfunctional acrylates in the blend so that there is extensive
cross-linking.

In the event the acrylate layers are applied by the evaporation and condensation
25 technique, the range of suitable acrylates is more restricted. These acrylate resins are
generally monomers having a molecular weight in the range of from 150 to 600. Preferably,
the monomers have a molecular weight in the range of from 200 to 400. Higher molecular
weight fluorinated acrylates or methacrylates may be equivalent to these lower molecular
weight materials and also be used for forming a deposited acrylate layer. For example, a
30 fluorinated acrylate with a molecular weight of about 2000 evaporates and condenses similar
to a non-fluorinated acrylate having a molecular weight in the order of 300. The acceptable
range of molecular weights for fluorinated acrylates is about 400 to 3000. Fluorinated
acrylates include monoacrylates, diacrylates, and methacrylates. Chlorinated acrylates may
also be useful.

35 If the molecular weight is below about 150, the monomer is too volatile and does not
condense well for forming a monomer film. If the molecular weight is more than about 600
the monomer does not evaporate readily in the flash evaporator at temperatures safely below
the decomposition temperature of the monomer.

40 When the monomers polymerize, there may be shrinkage of the film. Excessive
shrinkage may cause poor adhesion of the layer on the substrate. Shrinkage up to about 15
to 20% can be tolerated in the thin acrylate layers. However, it is preferred that the

1 shrinkage be less than 10% for reliable coating adhesion.

A typical monomer used for flash evaporation includes an appreciable amount of diacrylate and/or triacrylate to promote crosslinking. Blends of acrylates may be employed for obtaining desired evaporation and condensation characteristics and adhesion, and for
5 controlled shrinkage of the deposited film during polymerization.

Suitable monomers are those that can be flash evaporated in a vacuum chamber at a temperature below the thermal decomposition temperature of the monomer and below a temperature at which polymerization occurs in less than a few seconds at the evaporation temperature. The monomers selected should also be readily capable of crosslinking when
10 exposed to ultraviolet or electron beam radiation.

The monomer composition may comprise a mixture of monoacrylates and diacrylates. Triacrylates tend to be reactive and may polymerize at the evaporation temperatures. Generally speaking, shrinkage is reduced with higher molecular weight materials.

Generally, it is desirable that at least a major portion of the acrylate monomer
15 evaporated is a polyfunctional acrylate for crosslinking. Preferably, the acrylate comprises at least 70 percent polyfunctional acrylates such as diacrylate or triacrylate. If the degree of crosslinking is too low, the polymerized acrylate layer may not have adequate cure speed.

There are situations when less than half of the acrylate monomer comprises polyfunctional acrylates. For example, in a dry capacitor film one composition comprises
20 about 80% monoacrylate and 20% diacrylate. The high proportion of monoacrylate is used since it has a high dielectric constant.

Preferably, the molecular weight of the acrylate monomer is in the range of from 200 to 400. If the molecular weight is less than about 200, the monomer evaporates readily, but may not condense quantitatively on the substrate without chilling of the substrate. If the
25 molecular weight is more than about 400, the monomers become increasingly difficult to evaporate and higher evaporation temperatures are required.

Preferably, the acrylate monomer has a vapor pressure at 25°C in the range of from 1 to 20 micrometers of mercury. If the vapor pressure is less than about one micrometer, exceptionally high temperatures may be required to evaporate sufficient material for forming
30 a coating on the substrate in reasonable coating time. High temperatures may lead to thermal decomposition or premature curing of the monomers. If the vapor pressure is higher than about twenty micrometers of mercury, condensation of the monomer to form a film on the substrate may have too low an efficiency for practical coating operations. Adequate efficiency may not be obtained until the surface of the substrate is cooled below the freezing
35 point of the monomer, in which case the material may not polymerize properly.

There are at least five monoacrylates, ten diacrylates, ten to fifteen triacrylates and two or three tetraacrylates which may be included in the evaporated composition. Most preferably the acrylate comprises hexane diol diacrylate (HDDA) with a molecular weight of 226 and/or tripropylene glycol diacrylate (TRPGDA) with a molecular weight of about
40 300. Other acrylates may be used, sometimes in combination, such as monoacrylates 2-phenoxy ethyl acrylate (M.W. 192), isobornyl acrylate (M.W. 208) and lauryl acrylate

1 (M.W. 240), epoxy acrylate RDX80095 made by Radcure of Atlanta, Georgia; diacrylates
diethylene glycol diacrylate (M.W. 214), neopentyl glycol diacrylate (M.W. 212),
propoxylated neopentyl glycol diacrylate (M.W. 328) and polyethylene glycol diacrylate,
5 tetraethylene glycol diacrylate (M.W. 302), and bisphenol A epoxy diacrylate; and
triacrylates trimethylol propane triacrylate (M.W. 296), ethoxylated trimethylol propane
triacrylate (M.W. 428), propylated trimethylol propane triacrylate (M.W. 470) and pentaery-
thritol triacrylate (M.W. 298). Monomethacrylates isobornyl methacrylate (M.W. 222) and
2-phenoxyethyl methacrylate (M.W. 206) and dimethacrylates triethylene glycol dimethacry-
late (M.W. 286) and 1,6-hexanediol dimethacrylate (M.W. 254) may also be useful, but may
10 cure too slowly to be useful for high speed coating operations.

It has generally been considered that it is not feasible to evaporate high molecular
weight acrylates because of their very low vapor pressure and high viscosity. Evaporated
acrylate coatings have been restricted to low molecular weight monomers, generally below
a molecular weight of about 400 and with low viscosity. Generally the viscosities are below
15 50 centistoke.

It has been found, however, that by mixing a very low and a very high viscosity
material, flash evaporation, condensation and curing can be obtained. For example, a
mixture of 70 percent tripropylene glycol diacrylate (TRPGDA) and 30 percent of beta
carboxy ethyl acrylate (BCEA) has a viscosity of about 15 centistokes and can be readily
20 evaporated, condensed and cured. The low viscosity component lowers the viscosity of the
blend, which improves atomization in the evaporator and assists in the flash evaporation of
the high viscosity acrylate.

When blends of high and low molecular weight acrylates are used, it is preferred that
the weighted average molecular weight of the blend be in the range of from 200 to 600 and
25 preferably up to about 400. This assures that there is good vaporization of the blend at
reasonable temperatures in the evaporator.

Some examples of low molecular weight acrylates are hexane diol diacrylate,
diethylene glycol diacrylate, propane diacrylate, butane diol diacrylate, tripropylene glycol
diacrylate, neopentyl glycol diacrylate, phenoxyethyl acrylate, isobornyl acrylate and lauryl
30 acrylate. Some examples of high molecular weight acrylates are bisphenol A diacrylate,
BCEA, Radcure 7100 (an amine acrylate available from Radcure, Atlanta Georgia), Radcure
169, Radcure 170, acrylated and methacrylated phosphoric acid, Henkel 4770 (an amine
acrylate available from Henkel Corporation, Ambler, Pennsylvania) and glycerol propoxy
triacrylate.

35 Particularly preferred high molecular weight materials include BCEA which is acid
in character and has a shrinkage of only about 4 percent upon curing. Another suitable
material is an acrylate or methacrylate of phosphoric acid. One can also use acrylic acid in
the composition, along with dimers, trimers and tetrameres of acidic acrylates or
methacrylates. The molecular weight range of the acrylate may be extended by preheating
40 the prepolymer before it is atomized into the vaporization chamber.

It has been found that the temperature of the substrate on which the monomer film is

1 deposited can have a large influence on the efficiency of condensation. It is desirable to
refrigerate the substrate before it is placed in the vacuum chamber. Good condensation
efficiency can be obtained with monomers having a molecular weight of at least 200 with the
substrate cooled to temperatures in the range from 0 to 15°C. A rack of containers to be
5 coated can be removed from a refrigerator and placed in a vacuum chamber, pumped down
and coated before the containers warm to unreasonably high temperatures.

It is also desirable to cool the rotating drums so that the substrate remains at a low
temperature. When the sheet being coated is smooth and thin (generally less than 12
micrometers) good condensation efficiency can be obtained with monomers having a
10 molecular weight of at least 200 with the coating drum cooled to temperatures in the range
from 0 to 15°C.

Fig. 8 includes a series of data points showing measured condensation efficiencies of
hexane diol diacrylate monomer as a function of the substrate temperature. HDDA is a
relatively volatile monomer with a molecular weight about 212. A less volatile monomer
15 such as tripropylene glycol diacrylate with a molecular weight of about 300 has higher
condensation efficiency.

An extreme amount of cooling of the substrate must also be avoided. For example,
HDDA freezes on the substrate when the coating drum temperature is below about 0°C. The
frozen monomer cannot be polymerized. Thus, the cooling temperature must hold the
20 surface of the substrate above the freezing point of the monomer but below the temperature
at which the condensation efficiency decreases significantly.

As an alternative to or in addition to precooling the roll of substrate the sheet can be
cooled on the front surface preceding the evaporator. For example, the idler roll 42 between
the payout reel and the first drum may be chilled for cooling the front surface of the substrate
25 sheet before it reaches the first drum. Cooling the front face of the sheet, i.e. the face on
which deposition is to occur can permit faster processing and permits cooling of sheets with
a rough reverse surface.

Precooling of a sheet of material on which the acrylate is to be deposited can be
significant for applications in addition to preparation of sheet material for winding capacitors.
30 For example, there are times that it is desirable to coat paper with an acrylate and the rough
surface of paper does not lend itself to cooling from the back surface on a rotating drum.
In such a case, the flexible paper may be passed over a chilled roll to cool the front face of
the paper. An acrylate is then deposited on the same face of the paper as was just cooled
before the face heats any significant amount.

35 There may be embodiments where it is sufficient to deposit an oxygen barrier layer
directly on the substrate and apply an acrylate layer over the oxygen barrier material. For
example, when the thermoplastic substrate has been flame treated to smooth the surface
sufficiently that a thin oxygen barrier material can bridge over any surface irregularities, the
oxygen barrier material may be deposited directly on the flame treated substrate. An acrylate
40 layer may then be applied over the oxygen barrier material to protect the barrier and further
reduce permeability.

1 It is found particularly desirable to provide a protective crosslinked acrylate coating
over a deposited layer of metal such as aluminum. If an aluminum layer is applied to a sheet
substrate which is rolled for later use or which is passed over a roller contacting the surface,
the aluminum may be abraded off of higher asperities on the surface. A sheet coated with
5 aluminum and protected with an overlying crosslinked acrylate coating having a thickness of
as little as 0.1 micrometer, the pinhole density can be maintained as low as 10 pinholes per
cm².

When films used in packaging food products, cigarettes or many other items, the
presence of an acrylate odor is unacceptable. Any such odor can be eliminated by curing any
10 residual acrylate monomer on the film before it is removed from the vacuum chamber.

An electron gun 53 is mounted in the vacuum chamber between the final idler roll 42
and the take-up reel 41. Electron bombardment from the gun polymerizes any residual
acrylate monomer on the surfaces of the film before it is rolled up. By irradiating in the
converging space between the film on the take-up reel and the film advancing from the idler
15 roll both faces of the film can be irradiated with a single electron gun.

A sheet capacitor is often constructed by winding two sheets of metallized plastic sheet
together, with the metallized layer on one sheet being one electrode of the capacitor and the
metallized layer on the other sheet being the other electrode. The two sheets are offset from
each other so that at each end of the roll the edge of one sheet extends beyond the edge of
20 the other sheet. The electrical contact to the two electrodes is made by way of the protruding
edge of each electrode at opposite ends of the roll.

Molten zinc or lead-tin solder is then sprayed onto the ends of the roll (a process
called Schooping) to establish electrical contact with the metallized layer. A connecting lead
is either welded or soldered to the relatively thick contact material. The zinc or solder
25 Schooping apparently enters between the metallized plastic sheets and may melt a portion of
the sheet to make mechanical and electrical contact to the thin metallized layer on the sheet.

It is preferred to have a layer of polymerized acrylate overlying the metallized layer
of the capacitor material. A layer of acrylate in the range of from about 0.1 to 1 micrometer
thick has been found sufficient to prevent corrosion of a zinc electrode in a high humidity
30 environment. Furthermore, the overlying layer of acrylate improves the scratch resistance
of the metallized electrode. The electrode may be abraded during slitting of the metallized
sheet or winding a capacitor. An overlying acrylate layer effectively prevents damage from
such scratching. The overlying layer of acrylate also helps confine the tiny arc that occurs
adjacent to a short, which increases its temperature for more efficiently evaporating the metal
35 from around the shorted area. This, and the presence of oxygen in the acrylate material,
enhance the self-healing of the capacitor.

FIG. 9 illustrates in a fragmentary transverse cross section a few layers of a preferred
capacitor. Each of the layers of the capacitor comprises a substrate sheet 56 having a
metallized layer 57 on one face. A layer 58 of polymerized acrylate is deposited over each
40 metallized layer. A second acrylate layer 59 may be deposited on the opposite face of each
dielectric sheet 56 for isolating the sheet from dielectric capacitor liquid. A metal contact

1 electrode 60 is sprayed onto each end of the roll of metallized sheets.

The edges of the two sheets forming the capacitor are offset from each other. Thus, at one end of the capacitor, the edge of one sheet A extends beyond the edge of the intervening sheet B which is recessed. At the opposite end of the capacitor the recessed sheet
5 B extends beyond the edge of the interleaved sheet A. This permits electrical contact to be made to the metallized layers on the respective sheets at opposite ends of the capacitor.

In this embodiment the metallized layer on each sheet extends to one edge of the sheet and does not extend all the way to the opposite edge of the sheet. Thus, for example, as illustrated at the left edge of FIG. 9, the metallized layer extends all the way to the edge of
10 the protruding sheets A. On the other hand, the metallized layer on the recessed sheets B stop short of the edge of the sheet. Because of this, when the contact metal 60 is sprayed onto the end of the roll, electrical contact can be made to the metallized layer on the protruding sheet and the metallized layer on the recessed sheet is electrically insulated by the plastic material.

Surprisingly, despite the substantially complete enclosure of the metallized layer by acrylate and polypropylene plastic, good electrical contact is made when the electrical contact
15 is sprayed onto the end of the roll. It is believed that a small amount of thermoplastic dielectric sheet melts, thereby assuring good electrical contact with the metallized layer. Polypropylene has a melting temperature of about 165°C, and the cross linked acrylate does
20 not melt. The metallized layer is, in effect, supported by the polymerized acrylate which resists higher temperatures.

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WHAT IS CLAIMED IS:

1. A barrier with low oxygen permeability comprising:
a thermoplastic substrate;
5 a crosslinked acrylate layer on one face of the substrate; and
a layer of oxygen barrier material deposited on the same face of the substrate as the acrylate layer.
2. A barrier as recited in claim 1 comprising at least two acrylate layers, a first acrylate layer being under the oxygen barrier material and a second acrylate layer being over the oxygen barrier material.
3. A container with low oxygen permeability comprising:
a closable hollow container molded from a thermoplastic selected from the class
15 consisting of polypropylene, polyethylene, polyester and nylon;
a crosslinked acrylate layer on the outside of the container, the outside surface of the container being sufficiently smooth that the acrylate layer is continuous; and
a layer of oxygen barrier material deposited over the acrylate layer.
- 20 4. A method for forming an adherent barrier layer on a thermoplastic substrate comprising the steps of:
heating the surface of the substrate above its melting point;
depositing at least one liquid polyfunctional acrylate on the substrate;
polymerizing the acrylate for forming a crosslinked acrylate layer; and
25 depositing an oxygen barrier material over the crosslinked acrylate layer.
5. A method as recited in claim 4 wherein the heating step comprises exposing the substrate to a flame for a sufficient time to melt the surface of the thermoplastic material without deforming the substrate.
- 30 6. A method as recited in either one of claims 4 or 5 comprising the steps of:
chilling the substrate to a temperature below ambient temperature;
placing the chilled substrate in a vacuum chamber; and
condensing the acrylate monomer on the substrate while the substrate is still at a
35 temperature below ambient temperature.
7. A method for forming an acrylate polymer layer comprising the steps of:
preheating a polyfunctional acrylate prepolymer to a temperature above ambient temperature and lower than a temperature where the prepolymer polymerizes;
40 atomizing the prepolymer into a heated vaporization chamber in a vacuum system;
vaporizing the prepolymer in the vaporization chamber and discharging the vaporized

1 prepolymer into the vacuum system;
depositing the prepolymer on a substrate; and
polymerizing the acrylate prepolymer for forming a
crosslinked acrylate layer.

5

8. A method for forming an adherent acrylate layer on a substrate comprising the steps of:

plasma treating a surface of a substrate in a vacuum chamber, and immediately thereafter

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evaporating acrylate monomer having a molecular weight in the range of from 150 to 600, the acrylate monomer containing at least a portion of polyfunctional acrylate monomer for forming a crosslinked acrylate layer, and

condensing the acrylate monomer on the substrate as a monomer film; and
polymerizing the acrylate for forming a crosslinked acrylate layer.

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9. A method as recited in claim 8 comprising the steps of:

chilling a substrate to a temperature below ambient temperature;

placing the chilled substrate in a vacuum chamber; and

condensing the acrylate monomer on the substrate while the substrate is still at a
20 temperature below ambient temperature.

10. A method for making a barrier sheet with low oxygen permeability comprising the steps of:

plasma treating the surface of a polypropylene, polyester or nylon sheet substrate;

25 evaporating an acrylate monomer having a molecular weight in the range of from 150 to 600;

condensing such acrylate monomer on the treated face of the sheet substrate as a monomer film;

polymerizing the acrylate for forming a crosslinked acrylate layer; and

30

depositing a layer of oxygen barrier material selected from the group of silicon oxide, aluminum oxide and metal on the same face of the substrate as the acrylate layer.

11. A method as recited in claim 10 wherein the oxygen barrier material comprises a metal deposited over the acrylate layer and comprising the additional steps of:

35 evaporating an acrylate monomer having a molecular weight in the range of from 150 to 600;

condensing such acrylate monomer on the metal layer as a monomer film; and
polymerizing the acrylate for forming a second crosslinked acrylate layer.

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12. A method for forming a substrate coated with an acrylate layer comprising the steps of:

1 chilling a substrate to a temperature below ambient temperature outside of a deposition station;
passing the chilled substrate through a deposition station while the substrate is still at a temperature below ambient temperature;

5 at the deposition station:

evaporating an acrylate monomer having an average molecular weight in the range of from 150 to 600, and

condensing the acrylate monomer on the substrate as a monomer film; and
polymerizing the acrylate monomer film for forming a polymerized acrylate layer.

10 13. A method as recited in claim 12 wherein the substrate comprises a flexible sheet and comprising the steps of:

engaging a face of the flexible sheet with a chilled roller; and depositing the monomer on the same face that engaged the chilled roller.

15 14. A method as recited in either one of claims 12 or 13 wherein the substrate comprises a plastic film and comprising the steps of:

chilling a roll of plastic film,

unrolling the plastic film,

20 engaging the plastic film with a chilled drum, and

rotating the drum past the deposition station.

15 15. A method as recited in either one of claims 12 or 13 wherein the substrate comprises a flexible sheet film and comprising the steps of:

25 engaging a first face of the sheet with a chilled roller;

thereafter engaging the other face of the sheet with a chilled drum; and

rotating the drum past the deposition station for depositing acrylate monomer on the first face.

30 16. A method for forming a flexible sheet substrate coated with an acrylate layer comprising the steps of:

engaging a face of the flexible sheet with a chilled roller;

evaporating an acrylate monomer in a vacuum system;

condensing the acrylate as a monomer film on the same face of the substrate that was

35 engaged by the chilled roller; and

polymerizing the acrylate monomer film for forming a polymerized acrylate layer.

17. A method for forming an adherent acrylate layer on a substrate comprising the steps of:

40 evaporating a blend of acrylate monomers comprising at least one monomer having a molecular weight in the range of from 150 to 400 and an acrylate having a molecular

1 weight more than 600;

condensing the acrylate monomer blend on a substrate as a monomer film; and
polymerizing the acrylate for forming a polymerized acrylate layer.

5 18. The invention as recited in any one of the preceding claims wherein the oxygen
barrier material is selected from the group consisting of silicon oxide, silicon nitride,
aluminum nitride, titanium nitride, and aluminum oxide.

10 19. The invention as recited in any one of the preceding claims comprising at least
two acrylate layers, a first acrylate layer being under an oxygen barrier material and a second
acrylate layer being over the oxygen barrier layer.

20. A wound capacitor comprising:
at least one thermoplastic dielectric sheet wound into a cylinder;
15 a metallized conductive layer deposited on at least one face of the dielectric sheet;
a layer of crosslinked acrylate in direct contact with the entire metallized layer; and
an electrical contact made to the conductive layer at an end of the cylinder by
Schooping.

20 21. A capacitor as recited in claim 20 wherein the acrylate layer overlies the entire
metallized layer.

25 22. A capacitor as recited in claim 20 wherein the first layer of crosslinked acrylate
underlies the conductive layer and further comprising a second layer of crosslinked acrylate
deposited over the conductive layer.

30 23. A capacitor as recited in any one of claims 20, 21 or 22 further comprising a
second layer of crosslinked acrylate deposited on the face of the dielectric sheet opposite to
the face having the conductive layer.

24. A capacitor as recited in any one of claims 20, 21, 22, or 23 comprising a
dielectric fluid impregnating the cylinder.

35 25. A wound capacitor comprising:
a polypropylene or polyester dielectric sheet wound into a cylinder;
a layer of crosslinked acrylate deposited on a face of the dielectric sheet, the acrylate
layer being formed from acrylate monomer having a molecular weight in the range of from
about 150 to 600 and including at least a portion of polyfunctional acrylate molecules for
crosslinking;

40 a metallized conductive layer deposited over the acrylate layer;
a second layer of crosslinked acrylate deposited over the conductive layer; and

1 a dielectric liquid filling the capacitor.

26. Metallized capacitor sheet for forming a wound capacitor comprising:
a thermoplastic polypropylene or polyester dielectric sheet;
5 a metallized conductive layer deposited on at least one face of the dielectric sheet;
a first layer of polymerized acrylate deposited on the same face of the dielectric sheet
as the conductive layer; and
a second layer of polymerized acrylate deposited on the face of the dielectric sheet
opposite from the face having a conductive layer for isolating the dielectric sheet, the acrylate
10 layers being formed from acrylate monomer having a molecular weight in the range of from
about 150 to 600 and including at least a portion of polyfunctional acrylate molecules for
crosslinking.

15 27. The invention as recited in any one of the preceding claims wherein the acrylate
comprises an acrylate monomer having a molecular weight in the range of from 150 to 600.

28. The invention as recited in any one of the preceding claims wherein the acrylate
comprises an acrylate monomer having a molecular weight in the range of from 200 to 400.

20 29. The invention as recited in any one of the preceding claims wherein the acrylate
is a blend of acrylate monomers comprising at least one monomer having a molecular weight
in the range of from 150 to 400 and an acrylate having a molecular weight of more than 600.

25 30. The invention as recited in any one of the preceding claims wherein the acrylate
comprises a blend having at least one monomer selected from the group consisting of hexane
diol diacrylate, tripropylene glycol diacrylate, 2-phenoxy ethyl acrylate, isobornyl acrylate,
dicethylene glycol diacrylate, neopentyl glycol diacrylate, tetraethylene glycol diacrylate,
trimethylol propane triacrylate, pentaerythritol triacrylate, isobornyl methacrylate, 2-
30 phenoxyethyl acrylate, triethylene glycol dimethacrylate and 1,6-hexanediol dimethacrylate.

31. The invention as recited in any one of the preceding claims wherein the
monomers are selected from the group consisting of tripropylene glycol diacrylate, BCEA,
acrylates and methacrylates of phosphoric acid, acrylic acid and dimers, trimers and
35 tetramers of acidic acrylates or methacrylates.

32. A method as recited in any one of the preceding method claims wherein the
polymerizing step comprises irradiating the acrylate with radiation selected from the group
consisting of electrons and ultraviolet for forming a crosslinked acrylate layer.

40

Fig. 1

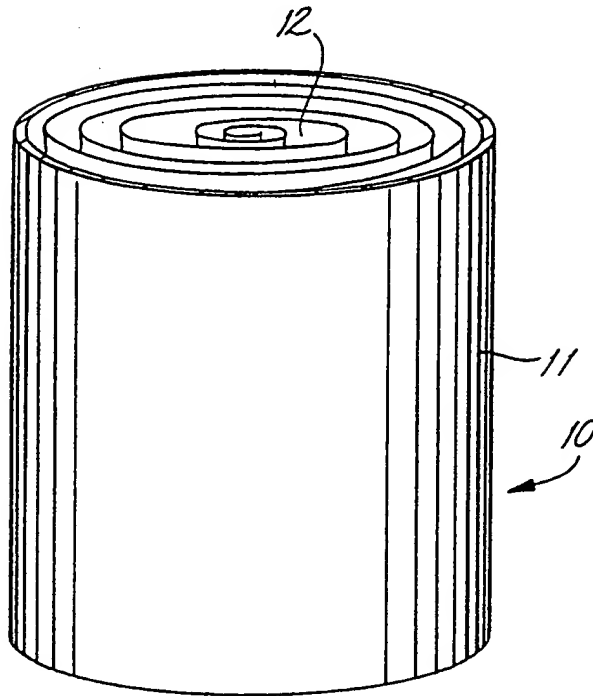


Fig. 2a

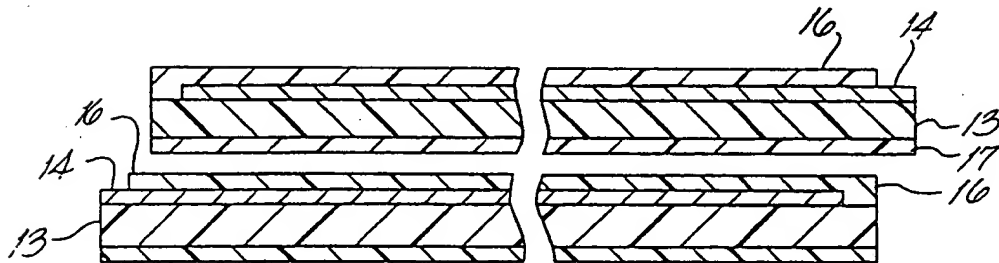


Fig. 2b

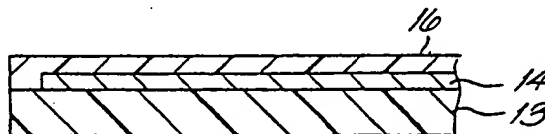


Fig. 2c

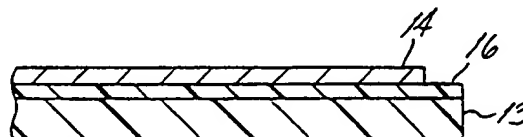


Fig. 3

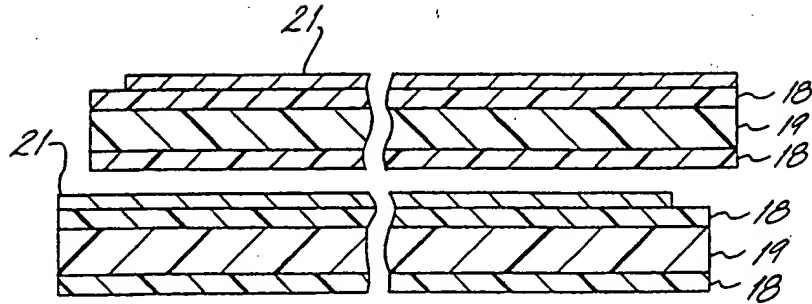


Fig. 4

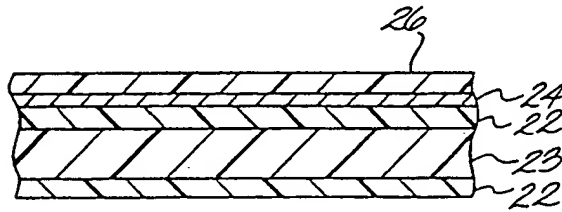
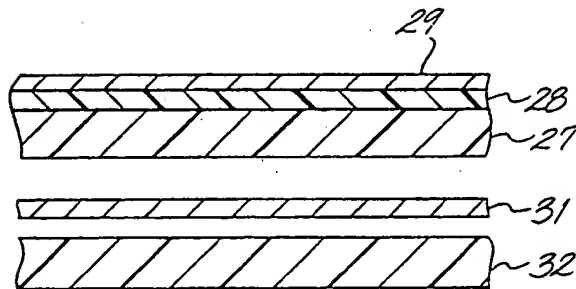


Fig. 5



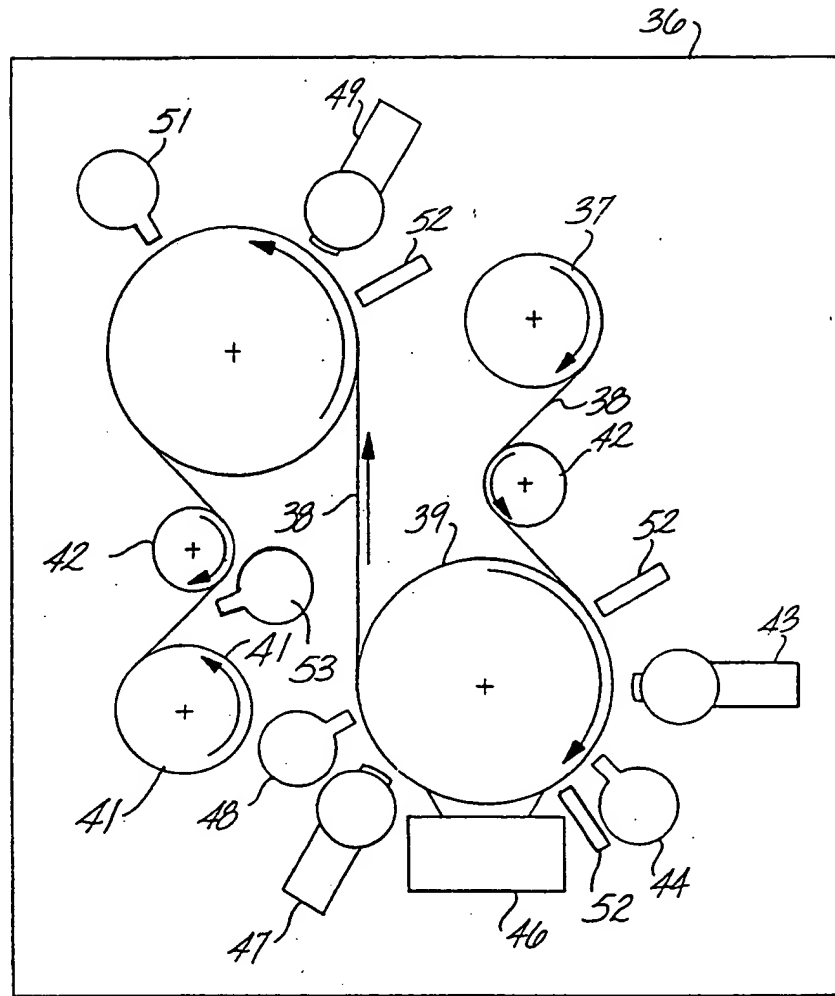


Fig. 6

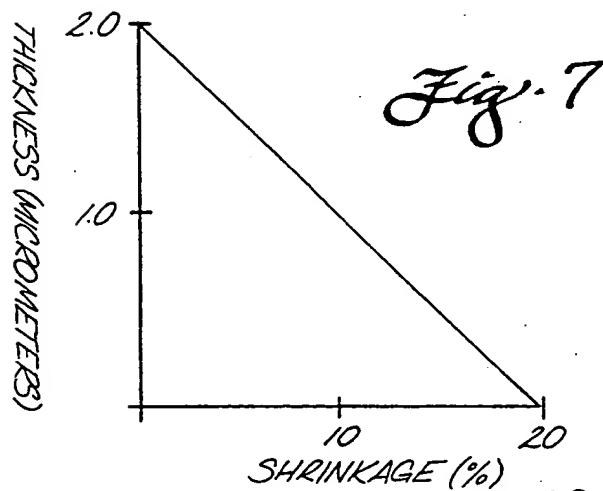


Fig. 8

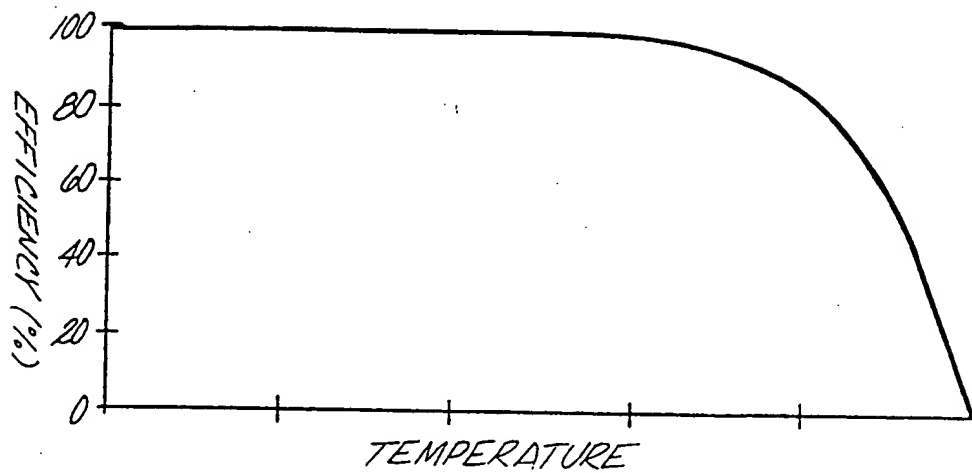


Fig. 9

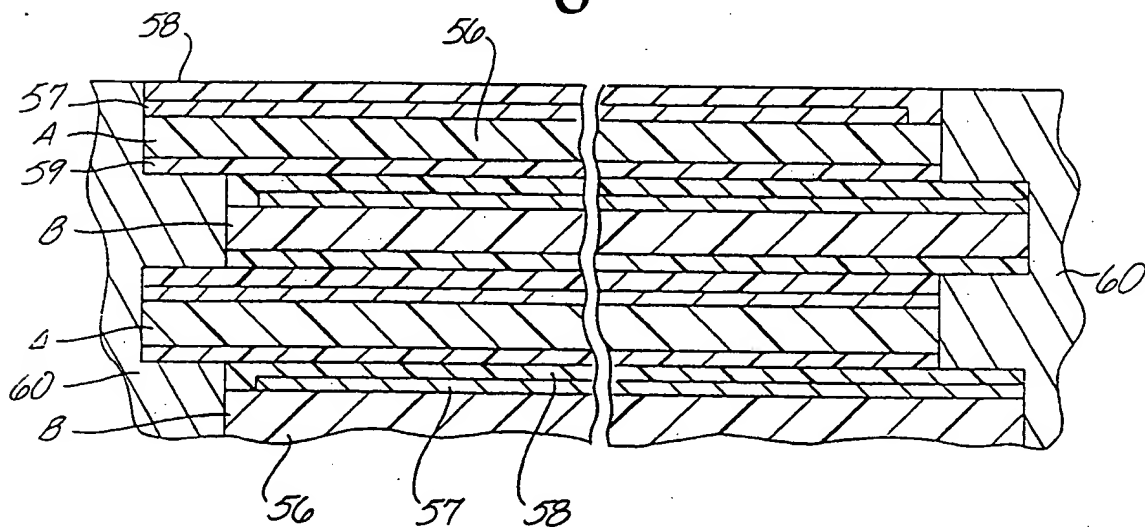


Fig. 10

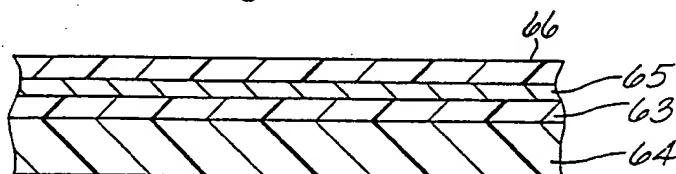


Fig. 11

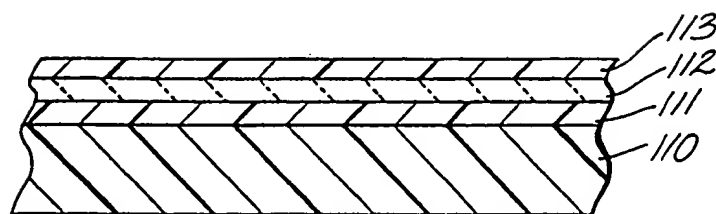


Fig. 12

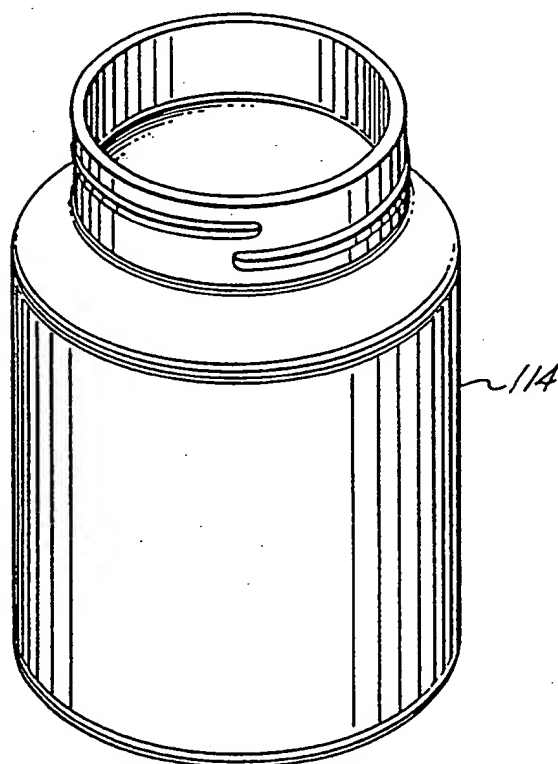


Fig. 13

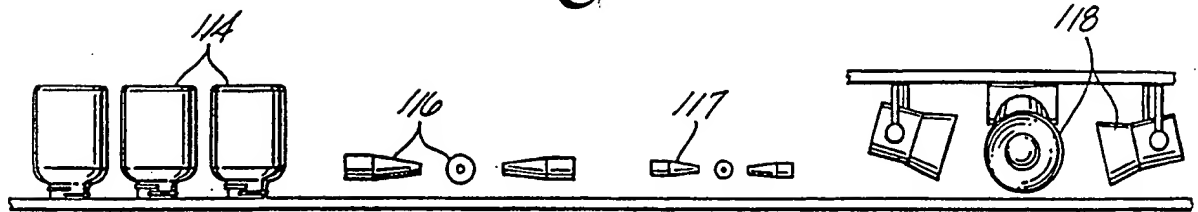
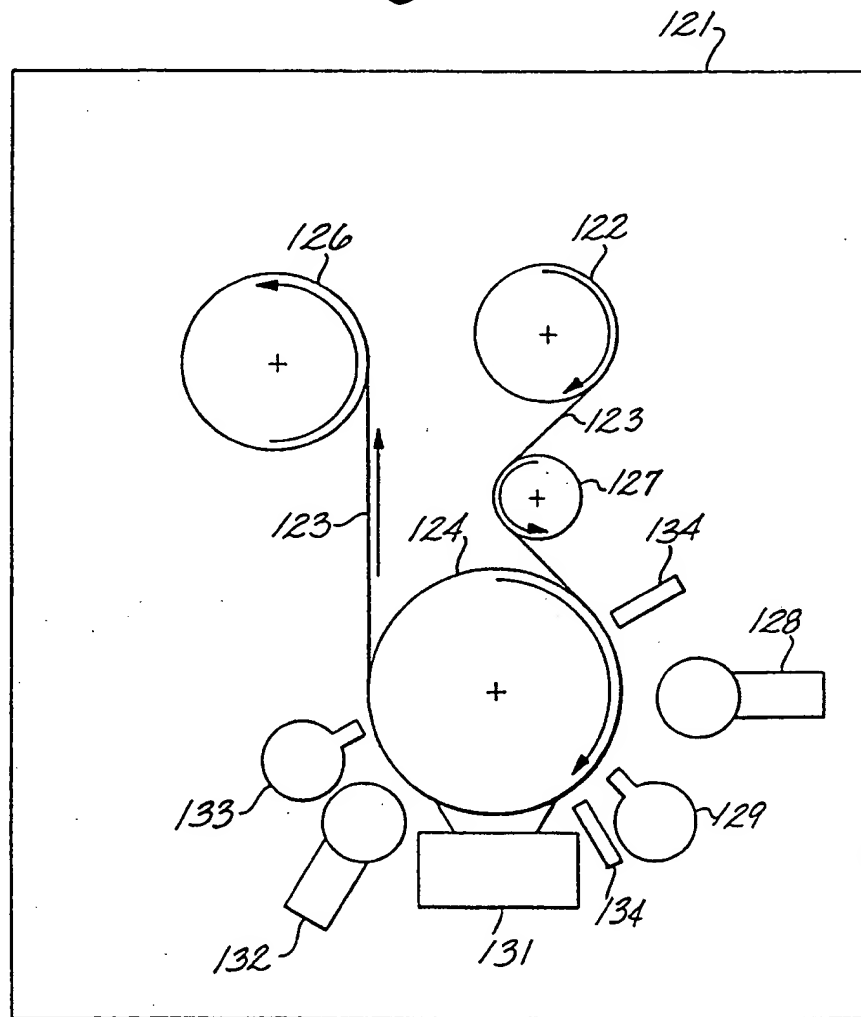


Fig. 14



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/11257

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :H01G 4/018, 4/32; B32B 27/28; B05D 3/08, 3/04; B65D 23/08

US CL :361/301.5, 323; 428/483; 427/535, 223; 215/12.2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: acrylate, crosslinked, oxygen barrier

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,993,811 (Walles) 23 November 1976, Figure 1.	3
Y	US, A, 4,229,777 (Merrill et al.) 21 October 1980, See entire document.	1,2,20-26
Y	US, A, 4,320,437 (Shaw et al.) 16 March 1982, col. 6, lines 22, 66.	1,2,20-26
Y	US, A, 4,499,520 (Cichanowski) 12 February 1985, col. 3, line 25.	30,31
A	US, A, 4,722,515 (Ham) 02 February 1988, See entire document.	1-32
Y	US, A, 4,728,701 (Jarvis et al.) 01 March 1988, col. 2, lines 7-20.	7

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
*A	document defining the general state of the art which is not considered to be of particular relevance		
*E	earlier document published on or after the international filing date	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O	document referring to an oral disclosure, use, exhibition or other means		
*P	document published prior to the international filing date but later than the priority date claimed	*G	document member of the same patent family

Date of the actual completion of the international search

11 JANUARY 1995

Date of mailing of the international search report

13 FEB 1995

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/11257

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,842,893 (Yializis et al.) 27 June 1989, See entire document.	1-32
Y	US, A, 4,919,985 (Asai et al.) 24 April 1990, col.1, lines 15-21.	3
A	US, A, 4,954,371 (Yializis) 04 September 1990, See entire document.	1-32
Y,P	US, A, 5,280,084 (Paul) 18 January 1994, col. 1, lines 20-30.	4-11

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/11257

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

361/301.5, 323; 428/483; 427/535, 223; 215/12.2; 361/272, 273, 275.1, 303, 304, 305, 308.1, 309, 311, 313, 314, 321.6, 327; 428/458, 480; 427/533, 314, 299, 561, 444; 215/1C, 12.1